# METALS DETERMINATION BY MICROWAVES DIGESTION AND ICP-AES TECHNIQUE OF UPGRADED LIQUIDS FROM HEAVY PETROLEUM RESIDS

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## INTRODUCTION

The utilization of heavy petroleum resids and heavy crudes inside the refinery has become one of the most important issues considered and studied by major oil companies. A simple way to utilize heavy fractions with high sulphur and metals' content is blending them with gasoil to produce a fuel to be burned in boilers or furnaces. This route however is becoming more and more difficult, because of increasing stringent environmental regulations. The present work is part of a research project concerning the utilization and the upgrading of heavy oils and of their residues. One of the objectives of the study is to define a process allowing the recovery from heavy resids of lighter and more valuable products which could be reutilized in the standard refinery cycle.

For the upgrading of the residues a continuous pyrolysis process has been considered. Pyrolysis tests, carried out in a rotary kiln system, were aimed to individuate best experimental conditions to maximize the production of liquid products and to increase their quality. The characteristics.of the fraction derived from the pyrolysis oils, in fact, must approach the specifications of conventional refinery unit operations, in order to lessen further upgrading treatments. Most of the refinery conversion and upgrading units presents severe limitation on the feedstock heavy metals' content. Therefore the presence of Ni and V in the liquids coming from the pyrolysis process results one of the most important parameters to be investigated to obtain a picture of products' quality.

Laboratory scale runs often produce small quantity of sample to be analyzed and quick responses are requested to direct experimental program. Alternative analytical procedures to traditional ASTM methods are to be defined in order to meet such requirements. Microwaves' digestion to dissolve liquid sample is an advantageous way to perform elemental analysis. The opportunity to work in closed vessels, under elevate pressures and controlled temperatures, avoids time consuming steps, such as incineration and sulphation, and experimental errors due to leaks of volatile compounds or sample contamination. This technique, coupled with an ICP-AES detection, has been emploied to determine Ni and V content in pyrolysis oils as described in this paper.

## EXPERIMENTAL

Two different feedstocks were tested: an Italian heavy crude, named "Gela", and the atmospheric residue deriving from the same crude (A.R. ex-Gela). Feedstocks characterization is reported in Table 1. A rotary kiln reactor was chosen to accomplish the pyrolysis step. This system allows to carry on continuous operations and to treat very high viscosity feedstocks. Agglomeration phenomena can be controlled and avoided by a proper optimization of plant operative conditions and by feeding a solid (e.g. sand, coke, dolomite) together with the liquid feed. Liquids feedrate is about 1 kg/h. Temperature, solid residence time and vapor residence time can be set for every run. The coke is discharged at the reactor exit and collected in a proper vessel. The vapor stream passes through two condensers, where the liquid products are separated, while the gas is filtered, metered ant burned in a flare. Gas samples can be collected after metering and off-line analyzed.

As said above, pyrolysis oil is the most important product. The oil is fractionated according to ASTM D-1160. The oil and the fraction are normally characterized to determine: elemental composition, bromine number (an index of the amount of olefins) for lighter fractions, density for lighter fractions, Conradson Carbon Residue for heavier fractions.

For the most significant runs, i.e. those yielding the largest amount of liquid products, the presence of Ni and V has been investigated. Liquid organic samples (up to 500 mg) have been directly mineralized using a microwaves' digestion system (CEM MDS 2000) which is able to simultaneously process up to twelve PFA closed vessels, under controlled pressure and temperature conditions. The dissolution goes through three subsequent steps involving oxidizing agents as $H_2SO_4$, $HNO_3$ and $HClO_4$.

The obtained clear solutions were analyzed by a sequential ICP-AE spectrometer (Perkin-Elmer Plasma 1000) equipped, when necessary, with an ultrasonic nebulizer (Cetac) to reach lower sensitivity, each element at its optimized condition of emission.

All the samples have been added of a proper amount of Sc solution as internal standard. A sample of a NIST standard fuel oil (1634c) was submitted to the same analytical procedure to verify the accuracy of the adopted method.

All the used reagents were of analytical grade of purity.

RESULTS AND DISCUSSION

*Pyrolysis tests*

Pyrolysis results showed that maximum liquids yield is obtained at a temperature of 500°C. Vapor residence time ($\tau_{gas}$) did not show pronounced effects on products distribution. However runs with higher residence time produced lighter, and therefore more valuable liquids. Table 2 shows products yield and fractions' distribution for two runs with A.R. ex-Gela and for the best run with Gela crude.

Pyrolysis oil is the main product in every run, yielding more than 50 wt. %. Gela test gives a higher liquid yield, being a less heavy feedstock compared to the atmospheric residue. 170-350°C fraction is the most important in all the pyrolysis oils obtained. Even if only a few runs are reported here, some results can be pointed out. The positive effect of an increased $\tau_{gas}$ is highlighted by the comparison between fraction distributions for run RATM10 and run RATM18. The latest ($\tau_{gas}$= 53 s) shows a distribution clearly shifted towards lighter fractions, concerning the run with shorter $\tau_{gas}$ (21 s). Fractions' characterization for the three runs are listed in Table 3. More details about overall mass balances and products analyses are reported elsewhere /1/.

*Analytical results*

Ni and V were determined on unfractionated pyrolysis oils and on the related distillation fractions. The adopted procedure utilizes the idea of subsequential oxidations performed by stronger and stronger agents. The optimization proceeded by varying microwaves' power, expressed as percentage of full scale, run time, reaction pressure and temperature.

All the samples were pretreated at the same way:

Up to 500 mg of sample was put in a PFA vessel and added with 2-3 ml of $H_2SO_4$. The vessel, opened, was then subjected to the following microwaves' steps:

| STEP | 1 | 2 |
|---|---|---|
| Power (%) | 20 | 0 |
| Run Time(min) | 20 | 20 |
| P (psi) | - | - |
| T (°C) | - | room |

Vessels: up to twelve

The $H_2SO_4$ (boiling point 330°C) is a strong oxidizing agent when hot. In this mild step it is preferred working with open vessel to reach higher temperature regarding those achievable under control by the optical fiber. After the treatment the sample looks like a "char".

The sample is then added of up to 10 ml $HNO_3$ and the closed vessel is put in the microwaves' system to undergo the following steps:

| STEP | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Power (%) | 40 | 60 | 70 | 90 | 0 |
| Run Time (min) | 15 | 15 | 15 | 20 | 0 |
| P (psi) | 80 | 120 | 160 | 200 | 20 |
| T (°C) | 80 | 120 | 160 | 185 | room |

Vessel: up to twelve

To the cool solutions 1-2 ml $HClO_4$ are added. The final digestion steps are following described:

| STEP | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Power (%) | 50 | 60 | 75 | 90 | 0 |
| Run Time (min) | 10 | 15 | 15 | 30 | 0 |
| P (psi) | 50 | 100 | 120 | 200 | 20 |
| T (°C) | 120 | 140 | 160 | 185 | room |

Vessel: up to twelve

The clear yellow solutions containing all metal perchlorates, very soluble in water, were then prepared to be analyzed by ICP-AES.

The described procedure, what's more it is based on simple analytical concepts of gradual oxidation, allows in a very short time (less than three hours) to process up to twelve samples having organic matrix, employing quite small amounts of reagents, and assuring prevention of leaks or external pollution.

The solutions were transferred into calibrated flasks, in which an aqueous solution of Sc was added. The Sc as internal standard is suggested by the instrument supplier to use the Myer-Tracy system /2/ which allows a more correct analyte determination as it reduces the short term noise and signal fluctuation due to the sample nebulization process. Ni and V were detected at $\lambda$=

231.604 nm and λ=309.311 nm respectively. The instrument calibration was performed utilizing three standard solutions and a blank containing all the same reagents present into the unknown solutions.

Results obtained on unfractionated oils and on respective distillation cuts are summarized in Table 4, together with mass balance to check the method's precision.

As expected metals concentrate in the heaviest cut. The small amount of Ni and V detected in the 170-350°C fractions seems quite unusual, with respect to conventional petroleum products, where metals are normally absent in lighter cuts. Moreover in 350-500°C fractions, metals are in fact almost absent. However repeated tests have confirmed present results. This particular aspect will be further investigated more thoroughly.

Mass balance data confirm the initial results and suggest the reliability of this method. The good comparison between the experimental data obtained applying the described procedure on a standard fuel oil and the certified values (Table 5) also guarantees the accuracy of the technique.

CONCLUSIONS

Upgradated liquid products have been obtained from heavy petroleum resids through a pyrolysis process. The presence of Ni and V in these products has been investigated using a particular technique of sample preparation and treatment. The method allows to treat small quantity of sample, prevents the occurrence of leaks oor external contamination and can process up to twelve samples in less than three hours. Results have been compared and validated by process mass balance and by the succesful application of the technique to a standard fuel oil.

REFERENCES

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/2/ Tiggelman, J.J., Oukes F.J. et al., Spectrochim. Acta, Part B, 1990, 45B(8), 927-32

**Table 1.** Feedstocks characterization.

|  | Gela crude | A.R. ex-Gela |
|---|---|---|
| *Elemental analysis (wt. %)* | | |
| Carbon | 81.11 | 81.49 |
| Hydrogen | 10.7 | 9.91 |
| Nitrogen | 0.41 | 0.56 |
| Sulphur | 7.42 | 7.97 |
| *Metals (ppmw)* | | |
| Nickel | 90 | 127 |
| Vanadium | 125 | 186 |
| *Conradson Carbon R. (wt. %)* | 12.86 | 18.13 |
| *Density at 15°C (g/ml)* | 0.9977 | 1.0892 |
| *Viscosity at 100°C (cSt)* | 115 | 2,177 |

**Table 2.** Pyrolysis products distribution.

| Run | T | $\tau_{gas}$ | $\tau_{solids}$ | Products (wt. %) | | | Liquid fractions (wt. %, oil basis) | | | |
|---|---|---|---|---|---|---|---|---|---|---|
|  | °C | s | min | gas | oil | coke | ibp-170 | 170-350 | 350-500 | 500°C+ |
| RATM10 | 500 | 21 | 30 | 39.3 | 51.2 | 9.5 | 6.67 | 45.40 | 31.50 | 16.33 |
| RATM18 | 500 | 53 | 30 | 37.5 | 50.7 | 11.8 | 16.91 | 60.98 | 16.08 | 6.02 |
| GELA3 | 500 | 50 | 30 | 30.5 | 58.4 | 11.1 | 16.53 | 49.93 | 23.89 | 9.65 |

Table 3. Characterization of the fractionated pyrolysis oils.

| | C | H | S | N* | n.Br** | CCR** | ρ** |
|---|---|---|---|---|---|---|---|
| | (wt. %) | | | | | (wt.%) | (g/ml) |
| RATM10 ibp-170 | 82.51 | 13.37 | 2.51 | 43 | 93.4 | | 0.7683 |
| RATM10 170-350 | 83.24 | 12.56 | 3.82 | 555 | 43.7 | | 0.8497 |
| RATM10 350-500 | 79.80 | 9.94 | 6.83 | 0.19 | | 0.75 | |
| RATM10 500°C+ | 81.46 | 8.51 | 8.46 | 0.39 | | 23.19 | |
| RATM18 ibp-170 | 83.25 | 13.32 | 1.55 | 56 | 85.7 | | 0.7566 |
| RATM18 170-350 | 83.22 | 12.34 | 4.04 | 912 | 48.3 | | 0.8410 |
| RATM18 350-500 | 82.43 | 9.92 | 7.29 | 0.23 | | 1.11 | |
| RATM18 500°C+ | 81.45 | 7.98 | 8.92 | 0.50 | | 29.12 | |
| GELA3 ibp-170 | 83.64 | 13.19 | 2.23 | 48 | 98.4 | | 0.7758 |
| GELA3 170-350 | 83.34 | 11.91 | 4.24 | 452 | 43.1 | | 0.8799 |
| GELA3 350-500 | 80.63 | 9.83 | 6.45 | 0.21 | | 0.83 | |
| GELA3 500°C+ | 80.67 | 7.72 | 8.99 | 0.42 | | 31.58 | |

\* = Nitrogen amount is expressed in ppmw for ibp-170 and 170-350 cuts; while it is wt. % for 350-500 and 500°C+ cuts.

** = Bromine number and density have been determined only for the lighter fractions. CCR has been determined only for the heavier fractions.

Table 4. Ni and V samples' content (ppmw) and mass balance.

| Run | Unfractionated oil | | Distillation cuts | | | | | | Sum of fractions | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | 170-350 | | 350-500 | | 500°C+ | | | |
| | Ni | V | Ni | V | Ni | V | Ni | V | Ni | V |
| RATM10 | 8.4 | 9.0 | 1.6 | 1.3 | 0.9 | <0.5 | 46.1 | 52.6 | 8.5 | 9.2 |
| RATM18 | 3.2 | 2.9 | 1.7 | 2.0 | <0.5 | <0.5 | 42.3 | 46.4 | 3.6 | 4.0 |
| GELA3 | 4.9 | 3.9 | 2.3 | 0.6 | 2.2 | <0.5 | 24.9 | 28.8 | 4.1 | 3.1 |

Table 5. Ni and V results (ppmw) on NIST standard: comparison between experimental and certified values (the expanded uncertainties are level of confidence of 95%).

| | NIST 1634C Standard Fuel Oil |
|---|---|
| Ni certified | 7.5 ± 0.2 |
| Ni experimental | 7.2 ± 0.4 |
| V certified | 28.2 ± 0.4 |
| V experimental | 28.3 ± 0.3 |

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